

holes and electrons in silver, as observed previously in gold and in platinum silicon thin films. In these prior art observations, the attenuation lengths of holes were a factor of approximately 1.5 smaller than for electrons. Additionally, sensitivity differences may be related to the energy spectra of holes and electrons excited by the surface reactions. The d-bands of bulk silver cannot contribute to the ballistic current, since they are more than 2.7 electron volts below the Fermi energy. The ballistic charge carriers thus have nearly a free SP character. The probability of exciting an electron-hole pairs is assumed to depend on the joint density of states of occupied and empty electronic states. Since the density of states of silver increases slightly with energy in the range of  $\pm 3$  electron volts around the Fermi energy, electrons closer to the Fermi energy are excited more effectively. Consequently, the energy distributions of ballistic holes and electrons are not symmetric around the Fermi energy and on the average the ballistic electrons are expected to have higher kinetic energies than hot holes. Such an asymmetry would lead to a significant sensitivity difference between p- and n-type diodes.

**[0042]** FIG. 3 is a graph of the chemicurrent as a function of time for atomic hydrogen and deuterium reacting with a 75 angstrom silver film on n-silicon (111). The oscillations in the decay curve for deuterium are due to plasma fluctuations. Although for the exposure graph of FIG. 3 the impingement rate of atomic deuterium was approximately twice as large as that for atomic hydrogen, the measured chemicurrent with deuterium exposure was smaller by a factor 3, i.e., a sensitivity to atomic deuterium is six times smaller than that to atomic hydrogen. The slight differences in the strengths of hydrogen and deuterium metal bonds cannot explain this observed isotope effect. A reduced adsorption probability for deuterium on silver would also not account for this observation, since this would affect the decay rate as well. The decay rates in FIG. 3 differ by a factor of approximately 1.8 which may be exclusively attributed to the flux difference between hydrogen and deuterium. The isotope effect implies different velocities and interaction times of the incoming hydrogen and deuterium by a factor of  $v^2$ . The interaction time, however, is still in the  $10^{-13}$  second range which is at least an order of magnitude longer than time constants of electron transfer between the substrate and the impinging atoms. For the same reason, we exclude internal exoelectron emissions which requires quenching of resonant charge transfer into the affinity level of the approaching atom accompanied by a drastic change of the surface oxidation state.

**[0043]** It is believed that the more relevant mechanism behind the isotope effect is likely to be the de-excitation of highly excited vibrational states formed under chemisorption. The transition probability between two vibrational levels in an anharmonic potential decreases the larger the difference of the two respective quantum numbers. Hence, de-excitation most likely occurs in multiple steps. The spacing between the vibrational levels, i.e., the density of states of vibrational states, determines the released energy in each step, and the states in the anharmonic deuterium-silver potential are closer to each other than for the hydrogen-silver bond. Since the formation energies of deuterium-silver and hydrogen-silver bonds are almost identical, the deuterium-silver vibrational energy may be relaxed in more steps of smaller energy quanta compared to the hydrogen-

silver case. This would result in ballistic charge carriers of lower energies and explain the smaller sensitivity to deuterium.

**[0044]** In summary, the foregoing disclosure is the first direct detection reported of hot electrons and holes excited by adsorption of atomic hydrogen deuterium on ultrathin silver and copper films as a chemicurrent. The current is measured in the large-area Schottky diode formed from these metals on oriented silicon (111). The devices are unique sensors that can discriminate atomic from molecular hydrogen as well as deuterium from hydrogen atoms. The chemicurrents decay exponentially with exposure time and reach a steady-state value. This behavior corresponds to occupation of free adsorption sites by hydrogen atoms and a balance between adsorption and abstraction. The currents are smaller if p-type semiconductors are used and if the devices are exposed to deuterium rather than hydrogen. This isotope effect opens a new way of monitoring reactions on metal surfaces and will certainly initiate further investigations to clarify the mechanism of the excitation. We have developed a reliable device structure for the fabrication of ultrathin Schottky diodes.

**[0045]** Many alterations and modifications may be made by those having ordinary skill in the art without departing from the spirit and scope of the invention. Therefore, it must be understood that the illustrated embodiment has been set forth only for the purposes of example and that it should not be taken as limiting the invention which could be more broadly or narrowly defined later by patent claims.

**[0046]** For example, it is expected that the chemoelectric phenomena associated with atomic and molecular interactions at metal surfaces will be found to show that chemical reactions at metal surfaces can directly transfer reaction energy to electrons in the metal. The phenomena can thus be utilized as the basis of a new class of solid state sensors. The adsorption induced current of different transition metal-semiconductor combinations will provide a means of systematically varying the relationships between the adsorbate and the metal surface and the electronic environment in the metal at the metal-semiconductor interface, and within the semiconductor. New sensor structures will have improved device sensitivity and allow discrimination of the electron energy with operation at room temperature and above. Bimolecular surface catalyzed reactions in addition to chemisorption is usable for direct excitation of charge carriers during formation of bonds between surface adsorbed species. In addition to the sensor performance and sensitivity for detection of hydrogen, several important adsorbates are possible expressly including CO, CO<sub>2</sub>, O<sub>2</sub>(0), N<sub>2</sub>(N), NO, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. FIG. 4 shows the chemisorption current as a function of time for CO with a 60 Angstrom Ag/n-silicon (111) sensor of the invention at 135K. FIG. 5 shows the chemisorption current as a function of time for CO with an 80 Angstrom Ag/n-silicon (111) sensor of the invention at 135K. FIG. 8 shows the response to molecular oxygen. Each adsorbate will have a unique current intensity and rate of signal decay which will allow differentiation of adsorbates.

**[0047]** The sensor response to surface catalyzed reactions of several combinations of these species following absorption are within the scope of the invention expressly including the reactions of CO+O<sub>2</sub>, CO+NO, and H<sub>2</sub>+O<sub>2</sub>. In the sensor